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VAPOR PRESSURES OF INORGANIC SUBSTANCES. XI GALLIUM.

by

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FOREWARD

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ABSTRACT

The vapor pressure of gallium has been determined by measuring the rate of fusion of the vapor through an orifice.

ΔH_0^o, the heat of sublimation of gallium at absolute zero, is 65.6 ± 0.5 kcal.

The vapor pressure data for gallium are represented by the equation

$$\log_{10} p \text{ (atm)} = 8.540 - \frac{1.200}{T} \times 10^4 - .844 \log T.$$

The normal boiling point, from this equation, is 2500° K.

INTRODUCTION

The only previous measurements of the vapor pressure of gallium were made by P. Harteck,[3] but since the purification of gallium is difficult and since considerable technological improvements in the preparation of gallium have been made in recent times, the vapor pressure of gallium has been redetermined. Furthermore, the possible use of gallium in high temperature heat engines gives added importance to the accumulation of accurate thermal data.

EXPERIMENTAL METHOD

APPARATUS AND PROCEDURE

The Knudsen method, the determination of the rate at which metal vapor at its equilibrium pressure effuses through an orifice, has been used throughout this research. The quartz vapor cell and the induction heating employed have been previously described.[4]

It was discovered that tantalum reacted with gallium at high temperatures. Consequently a quartz liner was made up for the tantalum Knudsen cell to contain the gallium. A convenient method of loading the Knudsen cell was to melt the gallium with hot water (m.p. 29.75° C.) and then to use a hypodermic needle to squirt the gallium through the 1/16" orifice into the cell. The vapor pressure of quartz was negligible at the highest temperature of these measurements.

Contrary to the observations of Harteck, no reaction of the gallium with quartz was noted. The surface of the gallium remained silvery and uncontaminated with the dark film observed by Harteck. The quartz liner was broken and examined to check this point at the conclusion of this research.

A disappearing filament optical pyrometer (Leeds and Northrup No. 8622) was used to measure the temperatures. The pyrometer was calibrated against a standard tungsten ribbon filament lamp

standardized by the National Bureau of Standards. The precision of the temperature measurements is 0.1 $^{o}/_{o}$.

SAMPLE

The sample was weighed with an accuracy of 0.02 mg.

The gallium used was obtained from the Eagle-Picher Lead Company. On the basis of spectroscopic analysis, the gallium contained 0.001 parts of lead and 0.002 parts copper. This corresponds to a purity of 99.75 mole percent.

It is possible to estimate the purity of the sample from premelting data obtained in determining the heat capacity in a low temperature calorimeter.[1] A purity of 99.96 mole percent is obtained by this method. Before making any vapor pressure measurements, the gallium was heated at 1350° K for several hours in a high vacuum to rid the sample of volatile impurities.

DATA AND DISCUSSION

The vapor pressure can be calculated from effusion data using the formula

$$p = m/k \sqrt{2\pi RT/M} . . . \qquad (1)$$

where p is the pressure in atmospheres, m is the rate of evaporation in g/sec/cm^2, T is the absolute temperature, M is the molecular weight of the vapor, R is the molar gas constant and k is the correction due to the resistance to free molecular flow owing to the thickness of the orifice. For an orifice radius of 0.55 mm and thickness 0.40 mm, k= 0 736.[2]

The experimental results are recorded in Table I. These pressures are 59 $^{o}/_{o}$ higher than those recorded by Harteck, although Harteck's data scatter sufficiently so that some of his data overlap those obtained in this research. The reason for this difference may be a consequence of the difference in purity of the gallium used or may, perhaps, be due to the fact that the gallium amalgamated with the platinum and chrom-nickel Knudsen cells that Harteck employed in his research.

TABLE I

THE VAPOR PRESSURE OF GALLIUM

$T^{0}K$	m $g \times 10^{3}$	Time Sec	$g/cm^{2}/sec$	Pressure Atm
1230	1.73	14,752	1.675×10^{-5}	1.588×10^{-6}
1234	5.98	31,265	2.733×10^{-5}	2.593×10^{-6}
1255	2.74	13,924	2.811×10^{-5}	2.690×10^{-6}
1267	2.64	5,918	6.374×10^{-5}	6.130×10^{-6}
1274	7.17	12,863	7.964×10^{-5}	7.678×10^{-6}
1284	3.18	7,036	6.457×10^{-5}	6.251×10^{-6}
1304	4.15	4,848	1.223×10^{-4}	1.193×10^{-5}
1309	4.03	6,931	8.308×10^{-5}	8.119×10^{-6}
1317	4.00	4,903	1.166×10^{-4}	1.143×10^{-5}
1327	3.29	3,318	1.417×10^{-4}	1.395×10^{-5}
1330	1.70	1,493	0.626×10^{-4}	1.602×10^{-5}
1345	3.54	1,740	2.907×10^{-4}	2.880×10^{-5}
1370	2.90	1,250	3.313×10^{-4}	3.313×10^{-5}
1372	7.52	3,122	3.442×10^{-4}	3.444×10^{-5}
1380	5.45	1,395	5.581×10^{-4}	5.601×10^{-5}
1385	9.71	3,367	4.120×10^{-4}	4.142×10^{-5}
1405	18.79	3,515	7.638×10^{-4}	7.733×10^{-5}
1425	21.51	3,369	9.122×10^{-4}	9.301×10^{-5}
1518	18.52	523	4.122×10^{-3}	4.339×10^{-4}

These vapor pressures have been computed upon the assumption that gallium vapor is monatomic.

The reliability of the vapor pressure data is best tested by establishing the invariance of ΔH_o^o (the heat of sublimation at absolute zero) in the thermodynamic relationship

$$R \ln p \text{ (atm)} = \left(\frac{F^o - H_o^o}{T}\right)_{liquid} - \left(\frac{F^o - H_o^o}{T}\right)_{vapor} - \frac{\Delta H_o^o}{T} \quad . . . (2)$$

when applied to the individual measurements of the equilibrium,

$$Ga(liquid) = Ga(vapor). \quad . . \quad (3)$$

The thermodynamic functions for the liquid are given by the expression

$$\left(\frac{F^o - H_o^o}{T}\right)_{liquid} = \frac{1}{T}\int_o^T C_p dT - \int_o^T C_p d\ln T. \quad . . \quad (4)$$

The following thermal data were used to calculate the thermodynamic functions for liquid gallium listed in column 2 of Table II.

Values for the thermodynamic functions up to 320° K were taken from previous calculations made in this Laboratory. These functions were extended into the high temperature range using a value of 6.645 cal/g atom/deg for the heat capacity of liquid gallium (determined at 320° K). The heat capacity of liquid gallium was assumed to be constant over the entire liquid range, and as a consequence there may be some error in the thermal functions for the liquid; however, this error should be quite small because the heat capacity for many liquid metals is virtually constant.

The free energy function for gallium vapor depends both on the vapor pressure and the energy states of the gallium vapor. The free energy function for the vapor is

$$\left(\frac{F^o - H_o^o}{T}\right)_{vapor} = -3/2 \, R \ln M - 5/2 \, R \ln T - C - R \ln R - R \ln Q. \quad . . \quad (5)$$

where M is the molecular weight of the vapor, $C + R \ln R = -7.267$ calories if p is expressed in atmospheres, $Q = \sum_i g_i e^{-\epsilon_i/kT}$ is the

TABLE II

THERMODYNAMIC CALCULATIONS FOR GALLIUM

$T^{o}K$	$-\left(\frac{F^{o} - H^{o}_{o}}{T}\right)_{liquid}$ cal/g atom/deg	$-\left(\frac{F^{o} - H^{o}_{o}}{T}\right)_{vapor}$ cal/g atom/deg	- Rln p(atm) cal/g atom/deg	ΔH^{o}_{o} kcal/g atom
1230	16.43	44.04	26.53	66.6
1234	16.50	44.05	26.56	66.8
1255	16.57	44.15	25.49	66.6
1267	16.64	44.19	23.85	65.1
1274	16.68	44.22	23.41	64.9
1284	16.74	44.26	23.81	65.9
1304	16.85	44.35	22.53	65.2
1309	16.87	44.37	23.30	66.5
1317	16.92	44.40	22.61	65.9
1327	16.98	44.44	22.22	65.9
1330	16.99	44.45	21.94	65.7
1345	17.07	44.51	20.78	64.9
1370	17.21	44.60	20.50	65.6
1372	17.22	44.61	20.42	65.6
1380	17.26	44.64	19.46	64.6
1385	17.28	44.66	20.06	65.7
1405	17.38	44.74	18.82	64.9
1425	17.49	44.81	18.45	65.2
1518	17.94	45.16	15.43	64.7
			Average	65.6 ± 0.5

partition function and g_i is the a priori weight of the state of energy ϵ_i; k is Boltzmann's constant.

All terms but the last on the right hand side of equation (5) are the translational contribution to the free energy function while the last term is the contribution due to the distribution of the gallium atoms among the available energy states of gallium at a given temperature. In the temperature range of these experiments only the ground state, $^2P^o_{1/2}$, and the first excited state, $^2P^o_{3/2}$, make an appreciable contribution to the internal energy of the vapor. Consequently,

$$Q = 2 + 4e^{-\epsilon_2/kT} \quad . \quad . \quad . \qquad (6)$$

where $\epsilon_1 = 0$ is the energy of the ground state and $\epsilon_2 = 826.6\ cm^{-1}$, is the energy of the first excited state.

The free energy functions for gallium vapor are tabulated in column 3 of Table II.

The ΔH^o_o values computed by equation (2) are given in the last column of Table II. These values show no temperature trend and are constant to within the experimental error of the vapor pressure data. The average value of 65.6 ± 0.5 kcal for ΔH^o_o is about 2 kcal lower than the value 67.7 calculated from the data of Harteck.[3] The heat of vaporization at the mean temperature (1350^o K) of these experiments is

$$\Delta H^o_{1350} = (H^o_{1350})_g - (H^o_{1350})_l + \Delta H^o_o = 6.7 - 9.7 + 65.6 = 62.6 \text{ kcal.} \quad . \quad . \quad (7)$$

Least squares treatment of our own data yields the following vapor pressure equation for gallium:

$$\log_{10} p(\text{atm}) = 8.540 - \frac{1.200}{T} \times 10^4 - .844 \log T \ldots \quad (8)$$

The boiling point of gallium, as computed from equation (8), is 2500^o K or 2227^o C.

This equation yields a value of 60.7 kcal for the heat of vaporization of liquid gallium, which differs by 1.9 kcal from the value obtained in equation (7).

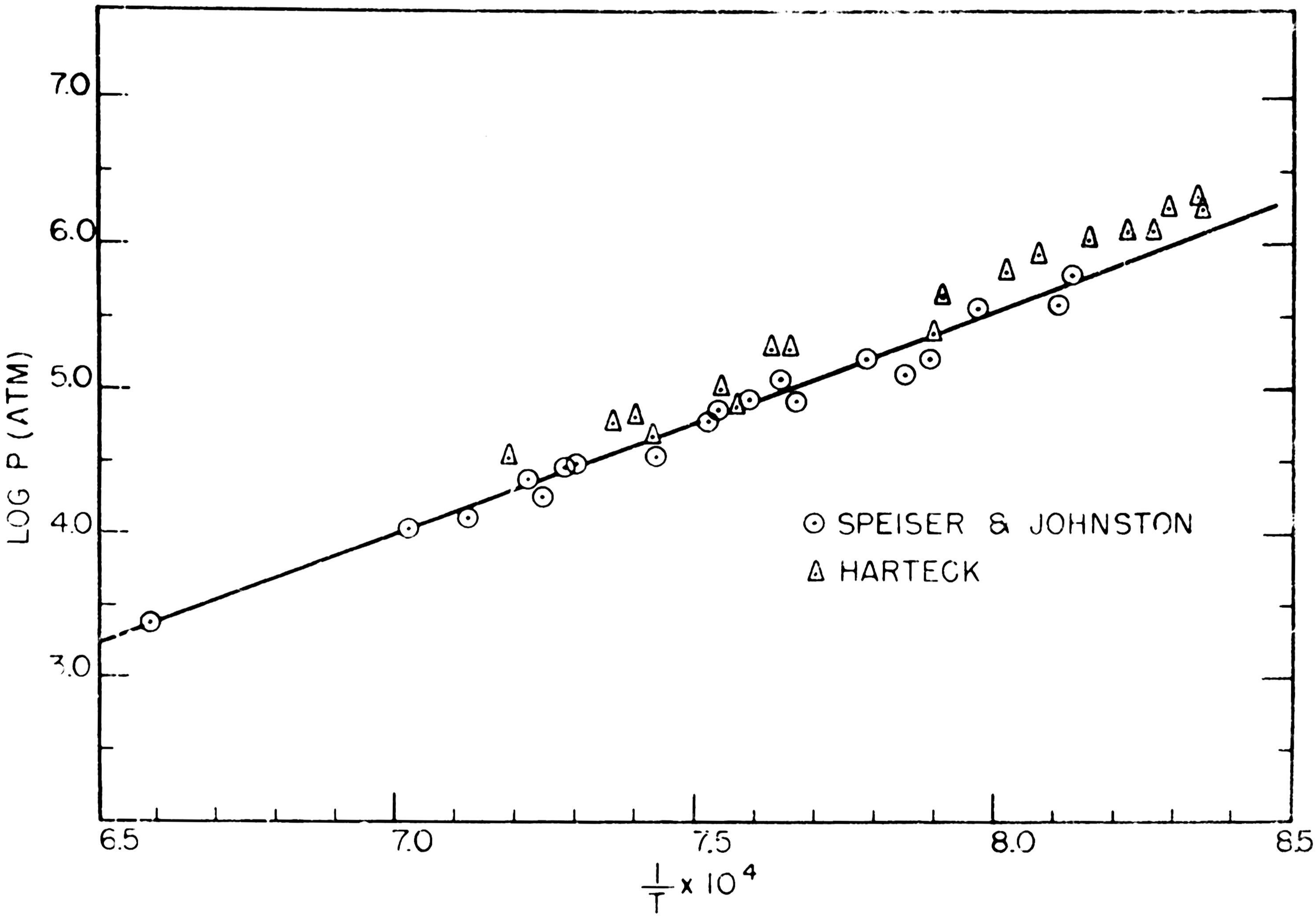

FIG. 1 GALLIUM; LOG P VS $\frac{1}{T}$

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